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HIGH PRESSURE ELECTRICAL CONDUCTIVITY STUDIES OF ACID
DOPED POLYBENZIMIDAZOLE

by

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**HIGH PRESSURE ELECTRICAL CONDUCTIVITY STUDIES OF ACID DOPED
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Abstract--Electrical conductivity studies of acid doped polybenzimidazole (PBI) and 85% phosphoric acid have been carried out. The PBI contained about 600 mol-% of 85% phosphoric acid and the electrical conductivity was deduced from complex impedance studies which were made at frequencies from 10 to 10^7 Hz. Measurements were made at pressures up to 0.25 GPa and temperatures of about 25, 50 and 75°C. Similar measurements were also carried out on 85% phosphoric acid. At room temperature the electrical conductivity decreases with increasing pressure for both acid doped PBI and 85% phosphoric acid. This behavior is expected for normal liquids and for ions in polymers where the viscosity increases with pressure. The resultant positive activation volume for the acid doped PBI has a magnitude similar to that for polymer electrolytes based on perfluorosulfonic acid containing relatively small amounts of water. Further, as temperature increases, the activation volume becomes smaller. Consequently, the acid doped PBI behaves like a polymer electrolyte where ion transport is mediated by segmental motions of the polymer. On the other hand, the activation volume at room temperature for 85% phosphoric acid is much smaller than for acid doped PBI. In addition, at 75°C the electrical conductivity increases with increasing pressure which gives rise to a negative activation volume. Consequently, there is very little similarity between the electrical behavior of the 85% phosphoric acid and of the acid doped PBI which were studied in the present work.

Key words: polybenzimidazole, electrical conductivity, high pressure, activation volume.

INTRODUCTION

In a recent paper Savinell et al. [1] proposed that polybenzimidazole (PBI) can be used as a polymer electrolyte in a polymer electrolyte fuel cell (PEFC) when it is doped with a strong acid such as 85% phosphoric or sulfuric acid. Those authors have shown that PBI exhibits good proton conductivity, low gas permeability, excellent oxidative and thermal stability and good mechanical flexibility at elevated temperature (200°C) [2-4] and have designed and tested hydrogen/air and direct methanol PEFCs utilizing PBI [2,5]. One very interesting feature of PBI is that it has an almost zero electro-osmotic drag coefficient [6] which simplifies fuel cell design. Because PBI is a promising PEFC material, fundamental studies of the electrical conductivity have been undertaken. In particular, studies of the effect of high pressure on the electrical conductivity have been carried out since they have been extremely useful in the study of other polymer electrolytes [7-11]. The results of the high pressure electrical conductivity studies for 85% phosphoric acid and acid doped PBI are reported in the present paper.

EXPERIMENTAL

Phosphoric acid (85%) doped PBI films have been prepared by 1) casting films from a dimethylacetamide solution which were subsequently equilibrated with 11M H_3PO_4 and 2) by direct casting from a solution of PBI and H_3PO_4 in a suitable solvent. The films used in this study were prepared by the latter method and contain 600 mol-% H_3PO_4 . For the high pressure measurements, the polymer samples were dried overnight at 60°C in a vacuum oven then transferred to a glove box for loading into a sample holder under relatively dry conditions.

The sample configuration was similar to that used recently for both gel electrolytes [10]. and Nafion ® [9]. Briefly, the samples were sealed inside viton rubber tubing using clamps on the ends. Platinum foil extended inside each end of the tubing to serve as electrical contacts for the sample. Hydrostatic pressures were generated using Spinesstic 22 spindle oil.

The phosphoric acid samples (85.8%, J. T. Baker, 0260-03) were prepared for measurement using techniques similar to those applied recently to both liquid electrolytes [10] and sulfuric acid [9]. Briefly, the 85% phosphoric acid was loaded into both 1/8 and 1/16 inch i.d. viton tubing. Stainless steel plugs were used in the ends of the tubing and consequently also served as electrodes. As a check on electrode effects, gold-coated stainless steel electrodes were also used.

Both the sealed liquid and polymer samples then clamped onto the closure plug of a high pressure vessel and connected to electrical feedthroughs. The equivalent parallel capacitance and resistance of the samples were determined using a CGA-83 Capacitance bridge (10 - 10^5 Hz) for most of the samples. In some cases, a Hewlett Packard 4194A Impedance/Gain-Phase Analyzer (10^4 - 10^7 Hz) was also used. All data were then transformed to the complex impedance, $Z^* = Z' - jZ''$. A platinum resistance thermometer was also located inside the pressure vessel so that in situ measurements of the temperature could be made.

RESULTS AND DISCUSSION

Electrical Conductivity

A typical complex impedance diagram for 85% phosphoric acid is shown in Fig. 1. The purpose of the plot is to show the data from two different measuring instruments. In general, an impedance arc, attributable to the bulk properties of the material, is observed at the highest frequencies. In addition, a slanted line, due to electrode effects, is observed at the lowest frequencies. Because of the wide

range of conductivity of the samples and different characteristics of the measuring instruments, different portions of the arc or line are observed for different samples at different temperatures and pressures. A second plot, shown in Fig. 2, shows the effect of high pressure on the complex impedance for acid doped PBI.

The data exhibit a slightly depressed semicircular arc, similar to that seen in other polymer electrolytes [8-11]. In the present work, all intercepts due to semicircular arcs were obtained graphically. The intercept of the impedance data with the Z' axis was taken to be the bulk resistance, R , of the sample. The conductance, $G=1/R$, was then calculated from the intercept and transformed to the electrical conductivity, σ , via:

$$\sigma = G\ell/A. \quad (1)$$

where A is the area of the sample and ℓ is the length.

The electrical conductivity of the 85% phosphoric acid at atmospheric pressure and room temperature is found to be about 0.08 S/cm. The electrical conductivity of the dry acid doped PBI (600 mol-%) sample used for the pressure studies was 4.5×10^{-5} S/cm. As is well known, the electrical conductivity of acid doped PBI depends strongly upon the amount of water in the sample [1]. While there is a wide variation in the electrical conductivity of the acid doped PBI depending upon the amount of water, it is clear that the electrical conductivity for the acid doped polymer is significantly less than for 85% phosphoric acid.

Electrical Conductivity vs. Pressure

Acid Doped PBI

The results for the variation of the electrical resistance with pressure for acid doped PBI at several temperatures are shown in Fig. 3 . It is found that the electrical resistance increases with increasing pressure at all temperatures for the material studied. Further, as temperature increases the variation with pressure decreases. This general trend is similar to the behavior observed for polymer electrolytes such as PPO [11]. In order to further compare acid doped PBI with those materials, the activation volume was calculated.

First, the pressure derivative of the resistance was converted to pressure derivative of the electrical conductivity using:

$$\left(\frac{\partial \ln \sigma}{\partial p}\right)_T = \frac{\chi_T}{3} - \left(\frac{\partial \ln R}{\partial p}\right)_T \quad (2)$$

where χ_T is the isothermal compressibility. Neither the compressibility of PBI nor 85% phosphoric acid is known. The compressibility of polymers is typically about $\chi_T=0.3/\text{GPa}$ [12] and that for water is $\chi_T=0.45/\text{GPa}$ [13]. Since the correction only amounts to about 5-10% a value of $\chi_T=0.3/\text{GPa}$ was used arbitrarily.

Finally, an activation volume was calculated from the pressure variation of the electrical conductivity via:

$$\Delta V = -kT \, d \ln \sigma / dp. \quad (3)$$

The results are given in Table 1. The values range from about 4 to 6 cm^3/mol . These values are somewhat smaller than the values observed in polymer electrolytes such as PPO [11]. However, they are similar to the values observed in polymer electrolytes based on perfluorosulfonic acid [8,9] containing less than

about 5 water molecules per sulfonate. It was concluded that ion motion at low water content (region i) in the perfluorosulfonic acid based materials was controlled by segmental motions of the polymer, presumably the pendant side chains [8,9]. On the basis of the available data, it is concluded that ion transport in the acid doped PBI studied in the present work occurs by a similar mechanism.

Phosphoric Acid

As can be seen by the data shown in Fig. 4, 85% phosphoric acid behaves differently. First, it is clear that the variation of the resistance with pressure at room temperature is much smaller than for acid doped PBI. In addition, there is a great deal of curvature in the semi-logarithmic resistance vs. pressure plot. More importantly, however, at 75°C, the resistance for 85% phosphoric acid decreases as pressure increases. At 55°C, the electrical resistance at first decreases then begins to increase as pressure increases.

In order to quantitatively compare these results with those for acid doped PBI an activation volume was calculated. Because of the curvature, a quadratic equation:

$$\ln(R/R_0) = ap + bp^2 \quad (4)$$

was best-fit to the data. The pressure coefficients, a and b , are listed in Table 1. The effect of pressure on the electrical conductivity was then calculated from equation (3). Due to the lack of a compressibility for 85% phosphoric acid, the value for water, $\chi_T=0.45/\text{GPa}$, was used [13]. It is clear that the effective activation volume at room temperature is much smaller for 85% phosphoric acid than for the acid doped polymer and for elevated temperatures, the activation volume is negative.

Negative activation volumes are not unusual. In fact, the activation volume associated with the electrical conductivity of water is negative. For example, on the basis of early data, Conway [14] concluded that the volume of activation is between -2.4 and -2.9 cm^3/mol . A more recent value as calculated from the data of Hamann [15] and presented by Holzapfel [16] is -10.6 cm^3/mol . Also, Quist et al. [17] found that for 0.002424 molal sulfuric acid at 70°C , $\text{dln}\sigma/\text{dp}=1.5/\text{GPa}$ which leads to a value of about -4.3 cm^3/mol . Finally, two of the authors have recently found negative activation volumes both for dilute sulfuric acid and for NAFION containing more than 10 water molecules per sulfonate [9].

It is relatively straightforward to devise a conductivity mechanism which will give rise to a negative activation volume. For example, proton motion in water is usually interpreted in terms of proton transfer from a hydronium ion, H_3O^+ , to a water molecule [14]. The activation volume for ion motion represents the volume change when a diffusing species transfers from a "normal" position to an "activated" position (sometimes referred to as the "saddle point"). For this mechanism, the "normal" state consists of two parts, a hydronium ion and a water molecule. The "activated" state may be thought of as a single system, two water molecules sharing a proton. Because of the sharing, the "activated" state would be expected to have a smaller volume than the "normal" state hence the negative volume of activation.

However, this model for the activation volume assumes that there is no change in the charge carrier concentration with pressure. In fact, that probably is not the case for 85% phosphoric acid. It is more likely that the negative activation volume at high temperatures is influenced by either the compressibility or the generation of charge carriers or both.

This can most easily be discussed in terms of the effect of pressure on the electrical conductivity, itself. Specifically, the electrical conductivity in a liquid can be written as [18]:

$$\sigma = (n_A z_A^2 \mu_A + n_B z_B^2 \mu_B) F^2 \quad (5)$$

where the μ_A and μ_B are the mobilities of ions A and B, n_A and n_B are the concentrations, z_A and z_B are the charge numbers and F is the Faraday constant. For the sake of simplicity, it will be assumed that there is only one type of charge carrier. This leads to the following approximation for the pressure dependence of the electrical conductivity:

$$\left(\frac{\partial \ln \sigma}{\partial p} \right)_T = \left(\frac{\partial \ln N}{\partial p} \right)_T + \chi_T + \left(\frac{\partial \ln \mu}{\partial p} \right)_T \quad (6)$$

where N is the number of charge carriers.

Further, the mobility can be rewritten in terms of viscosity, η via Stokes law:

$$\mu = \frac{N_A}{6\pi\eta r} \quad (7)$$

Equation (7) is based on the assumption that the size of the moving object is much larger than the size of the particles which make up the medium that it is moving through. Of course, this is not strictly valid for ions moving through 85% phosphoric acid, however, it provides a framework for discussing the effect of pressure on the electrical conductivity since equation (7) leads to:

$$\left(\frac{\partial \ln \sigma}{\partial p} \right)_T = \left(\frac{\partial \ln N}{\partial p} \right)_T + \chi_T - \left(\frac{\partial \ln \eta}{\partial p} \right)_T \quad (8)$$

Using either equations (6) or (8) it is straightforward to understand the negative pressure derivative of the electrical conductivity which is observed for 85% phosphoric acid at room temperature. If the mobility decreases or the viscosity increases with pressure, as is reasonable, all that is necessary is for the last term to dominate. This condition also applies to the acid doped PBI. That is reasonable since micro-Brownian motions of the polymer chain are often discussed in terms of viscosity [19].

It is also straightforward to understand the increase in electrical conductivity as pressure increases for 85% phosphoric acid at elevated temperatures. Part of the increase in electrical conductivity with pressure can be accounted for by the second term on the right hand side of equations (6) and (8), the isothermal compressibility, which represents an increase in the concentration (density) of charge carriers because the volume decreases as pressure increases. Unfortunately, the compressibility for 85% phosphoric acid at elevated temperature does not seem to be available. However, the compressibility of water, 0.45/GPa, is only slightly smaller than $d\ln\sigma/dp$ at 78°C. Consequently, most of the positive effect of pressure can be accounted for on the basis of the compressibility. However, this assumes that there is no effect of pressure on the viscosity or mobility. If the third term in equations (8) is positive, for example, there will be a residual positive pressure derivative of the electrical conductivity at elevated temperatures. This could then be explained via the first term in either equations (6) or (8) by letting the number of charge carriers increase as pressure increases. However, it is possible that the mobility could increase or the viscosity decrease as pressure increases. This is a well known phenomenon in water [20,21] and is interpreted as pressure breaking the local structure of water thereby making it easier for ion or molecular motion.

Unfortunately, at present no data appears to exist concerning the various terms on the right hand side of equations (6) and (8) and thus no definitive statements can be made concerning the magnitudes of the various contributions to the variation of electrical conductivity with pressure. However, it is clear that a reasonable interpretation of the data will be possible.

Finally, it is important to keep in mind that the present high pressure work has been limited to acid doped PBI with one water content and one 85% phosphoric acid content. In addition, only 85% phosphoric acid has been studied. While the comparison of the two materials is interesting, it would be premature to generalize at the present time. It will be of interest to extend the pressure work to other acid and/or water contents as well as to both higher and lower temperatures.

CONCLUSIONS

Electrical conductivity studies of acid doped PBI and 85% phosphoric acid have been carried out at high pressures and temperatures. At room temperature the electrical conductivity decreases with increasing pressure for both acid doped PBI and 85% phosphoric acid. This behavior, with a positive activation volume, is that expected for "normal" liquids and for ions in polymers. In fact, the size of the activation volume for the acid doped PBI is similar to that for polymer electrolytes based on perfluorosulfonic acid containing relatively small amounts of water. Further, as temperature increases, the activation volume becomes smaller but remains positive for the acid doped polymer. Consequently, the acid doped PBI behaves like a true polymer electrolyte where ion transport is mediated by segmental motions of the polymer. On the other hand, the activation volume at room temperature for 85% phosphoric acid is much smaller than for acid doped PBI. In addition, for 85% phosphoric acid at 75°C the electrical conductivity increases with increasing pressure which gives rise to a negative activation volume. Consequently, there is very little similarity between the 85% phosphoric acid and acid doped PBI which were studied in the present work.

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Table 1. Effect of pressure on the electrical conductivity for 600 mol-% acid doped PBI and 85% phosphoric acid.

Temp.	R_0	a	b	$\frac{\chi T}{3}$	$\frac{\partial \ln \sigma}{\partial p}$	ΔV
(°C)	(Ohms)	(GPa) ⁻¹	(GPa) ⁻²	(GPa) ⁻¹	(GPa) ⁻¹	(cm ³ /mol)

Acid Doped PBI

24	3.9x10 ⁶	2.65		0.1	-2.55	+6.3
51.5	4.9x10 ⁵	2.00		0.1	-1.90	+5.1
76.6	1.2x10 ⁵	1.45		0.1	-1.35	+3.9

Phosphoric Acid

26	2305	+0.20	0.94	0.15	-0.05	+0.12
57	1149	-0.20	1.0	0.15	+0.35	-0.96
78	803	-0.40	0.68	0.15	+0.55	-1.6

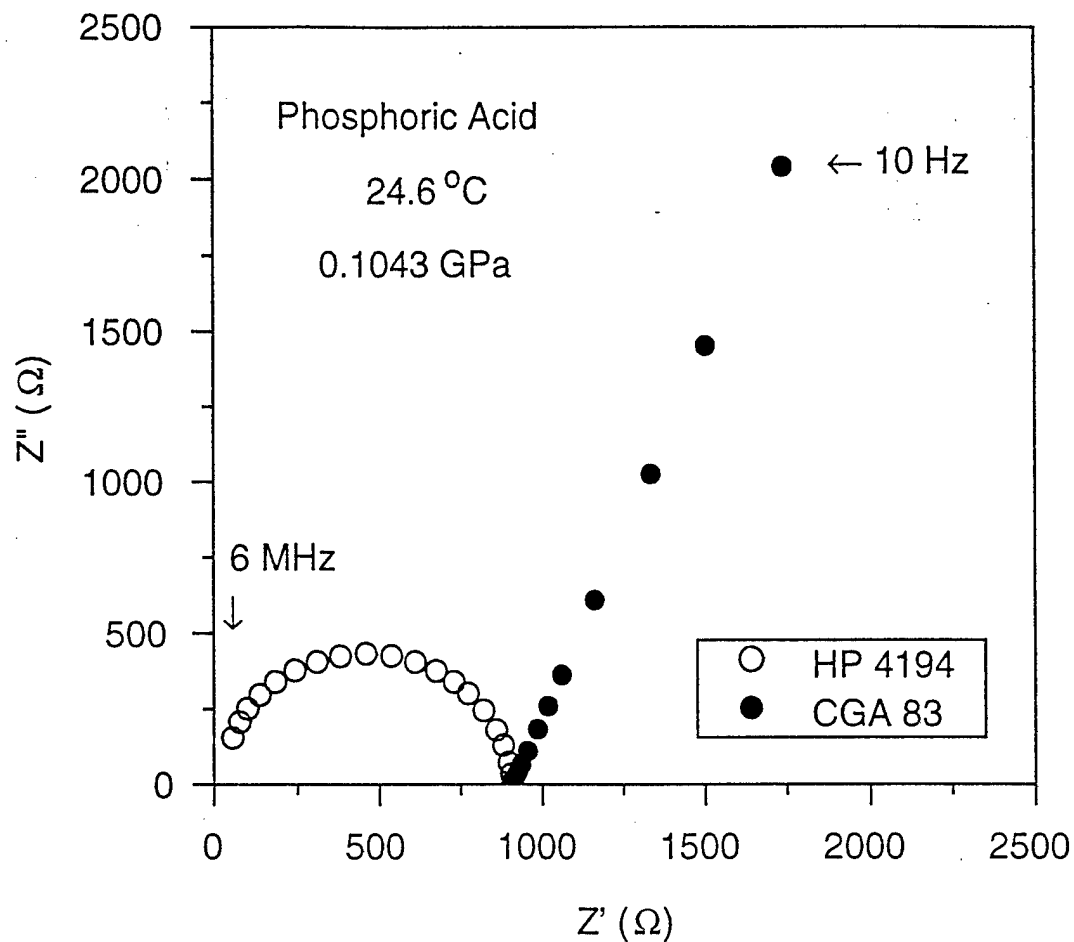


Figure 1. Complex impedance diagram at 24.6°C for 85% phosphoric acid. The solid circles represent data from the Hewlett Packard 4194 and the open circles are data obtained from a CGA-83 Capacitance bridge. The frequencies increase from right to left.

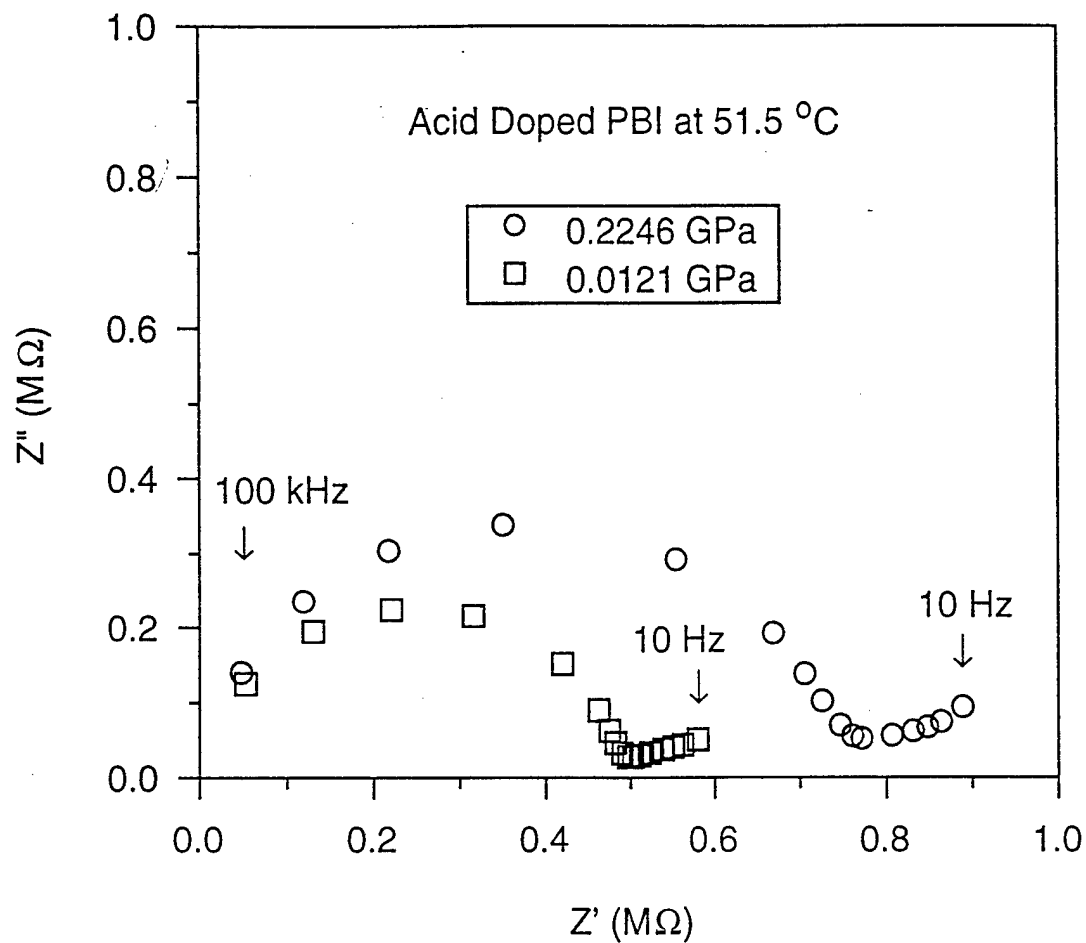


Figure 2. Complex impedance diagrams at 51.5°C and two pressures for acid doped PBI. The open circles (0.2246 GPa) and open squares (0.0121 GPa) represent datum points obtained using a CGA-83 Capacitance bridge. The frequencies increase from right to left and the frequency range is 10 to 10⁵ Hz.

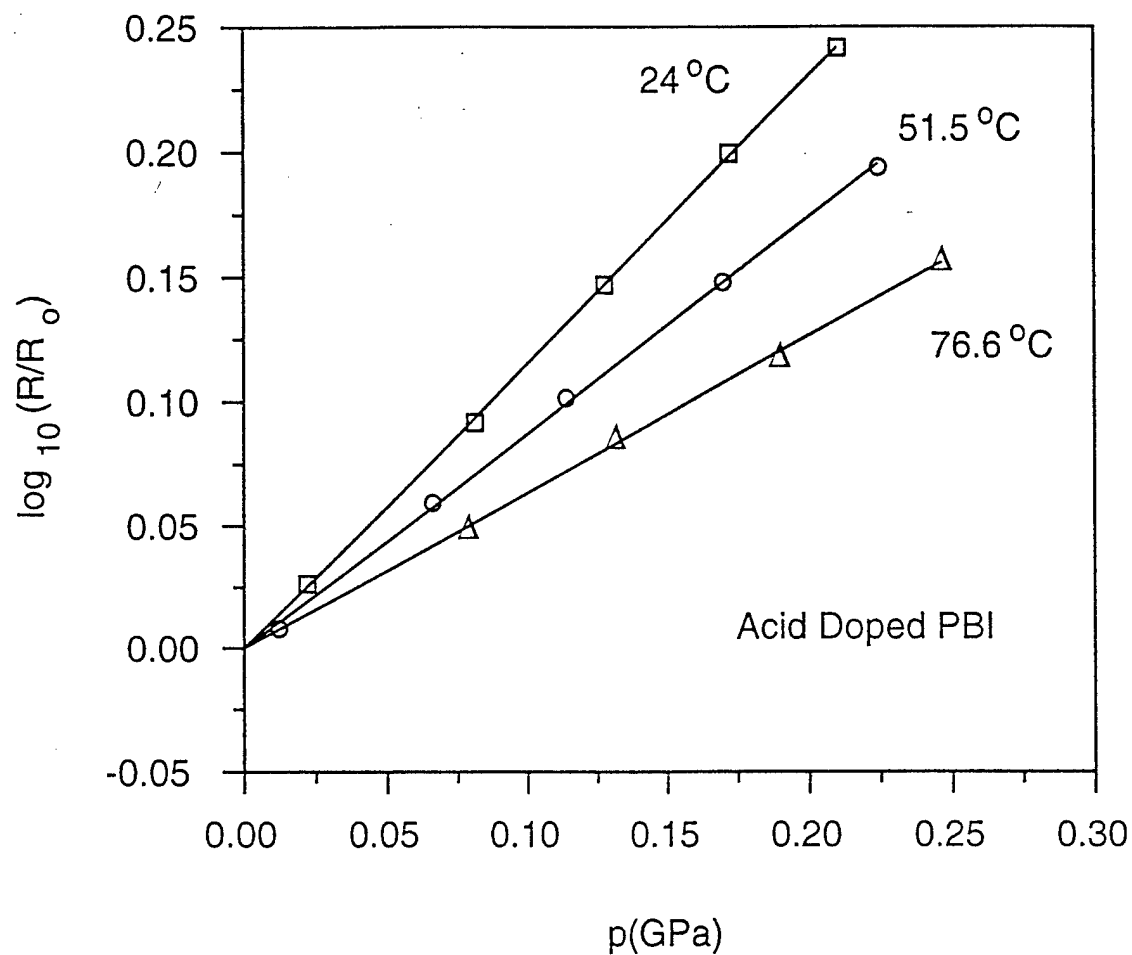


Figure 3. Relative electrical resistance vs. pressure at various temperatures for acid doped PBI. Also shown are the best-fit straight lines.

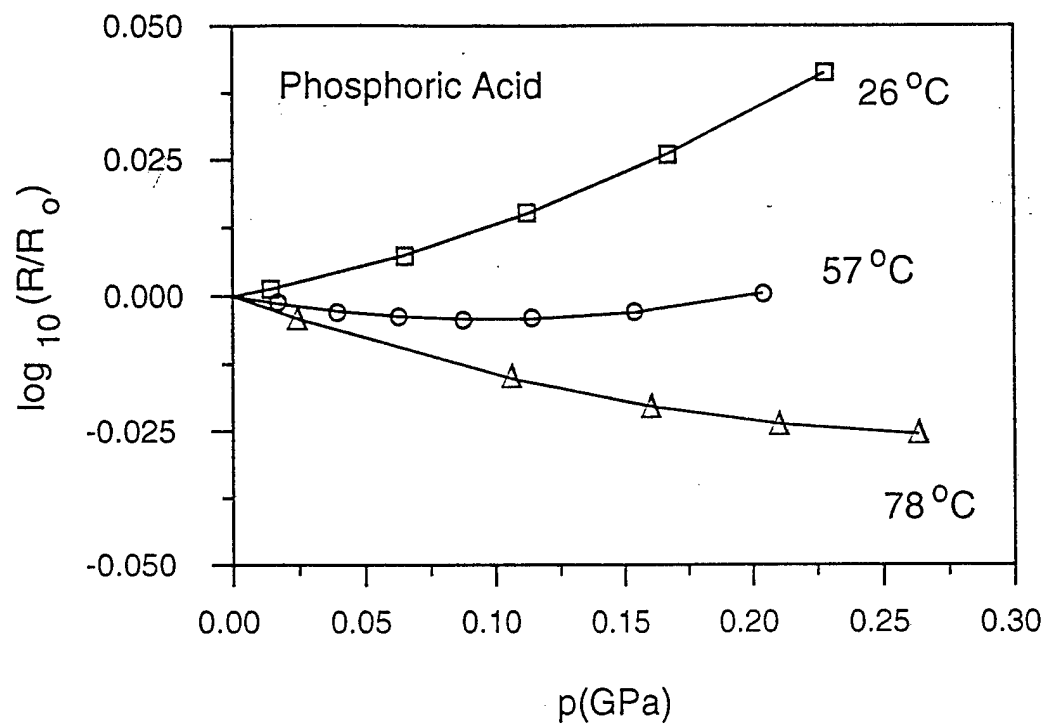


Figure 4. Relative electrical resistance vs. pressure at various temperatures for 85% phosphoric acid. Also shown are the best-fit quadratic equations.